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Vapor-grown carbon fiber anode for cylindrical lithium ion rechargeable batteries

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Abstract

A lithium ion rechargeable battery based on carbon anode that is a viable replacement for lithium metal anode has been developed. In this investigation, the *Vapor-Grown Carbon Fiber* was used as the anode material of a cylindrical battery. The charge/discharge experiments were carried under various temperatures and current densities. Excellent cyclability was obtained at 21°C at a charge/discharge of 0.8 C with three cathode materials ($LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$). High discharge capacity was obtained at low temperature (0°C). Good cyclability was also obtained at high temperature (40°C). At the charge/discharge rate of 4.0 C, energy density did not decay significantly. Good cyclability was obtained for rates ranging from 0.8 C to 4.0 C. Self-discharge was investigated at 3 temperatures (21, 40 and 60°C). The measured self-discharge was 8, 15 and 31% per month at 21, 40 and 60°C, respectively.

Keywords: Lithium ion; Vapor-Grown Carbon Fiber; Charge/discharge

1. Introduction

New generation high energy, Li-ion rechargeable batteries have attracted a great deal of attention. Until now, many types of carbon materials have been investigated as the negative electrode for these batteries. Vapor-Grown Carbon Fiber (VGCF) is a soft, fibrous carbon material. The crystallinity of this material after graphitization is close to that of single crystal graphite. Further, VGCF consists of concentric layers of basal plane graphite with fiber diameter, length, and aspect ratio that can be changed by process control. At the 7th International Meeting on Lithium Batteries (Boston, 1994), effects of VGCF preparing method on electrochemical performance were discussed, and electrochemical behaviors with various electrolytes were presented [1,2]. VGCF showed high capacity (> 360 mAh/g) and high cyclability. Moreover, the coulombic efficiency of the first cycle can be improved by controlling the fiber length of VGCF [3]. Therefore, VGCF is regarded with keen interest as a promising candidate carbon anode for Li-ion rechargeable batteries.

We have developed a new, improved Li-ion rechargeable battery using VGCF as anode material. VGCF/4V Li-ion batteries (A-size, diameter = 16 mm, height = 50 mm) were tested. Recently, 8 A h cells were constructed in order to enter the electric-bicycle market. In this paper the key materials for this cell and construction of cells are discussed. The properties of this cell, such as charge/discharge characteristics, temperature dependence on discharge capacity, self-discharge, cyclability, and comparison with commercial Li-ion batteries are also covered. In the conclusion, the characteristics of Nikkiso's lithium-ion rechargeable batteries are summarized.

2. Experimental

VGCF (Grasker™, produced by Nikkiso) heat-treated at 2800°C was used as the anode material. SEM image of VGCF is shown in Fig. 1a. The VGCF consists of short-fiber graphite as seen in Fig. 1a. The VGCF cross-section (as grown), shown in Fig. 1b, displays the concentric layers of basal plane graphite of the material.

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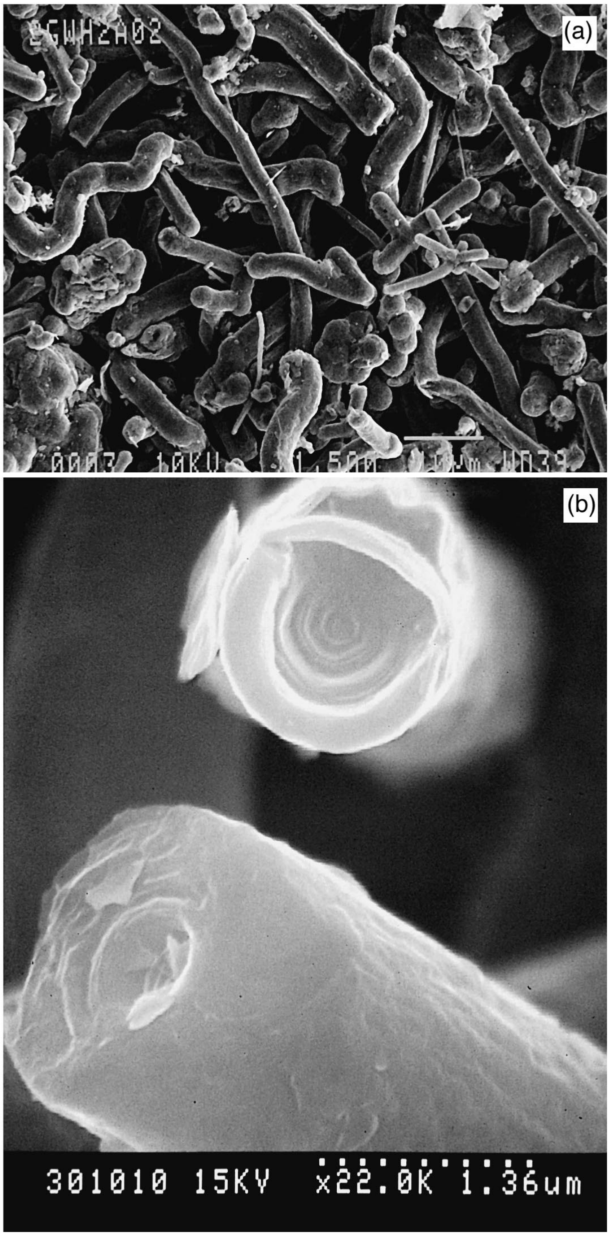

Fig. 1. (a) SEM micrograph of VGCF heat-treated at 2800°C. (b) SEM micrograph of the cross-section of a VGCF heat-treated at 1000°C.

The VGCFs were prepared from hydrocarbons by a vapor-growth method and chopped to ca. 10 μm in length by a hybridizer. The chopping process snapped the VGCFs repeatedly by rapidly rotating the fine plates of the hybridizer until their length was 10 μm. Three different types of the VGCFs were chosen with nominal diameters of 1, 2, and 3 μm (1GWH, 2GWH, and 3GWH, respectively). Two procedures were examined to prepare the chopped VGCFs. In the normal procedure (1A), the VGCFs were graphitized after the chopping process; in the other process (2A), they were chopped after graphitization. For this study we chose 2GWG-2A (2 μm in diameter and 10 μm in length).

The reversible capacity of this carbon was 328 mAh/g-carbon. The coulombic efficiency reached 93% at the first cycle in a three-electrode cell at a current density of 25 mA/g of VGCF. The anode material was mixed with poly-[vinylidene fluoride] (PVDF) as binder. The mixture was spread on a copper sheet. $LiCoO_2$ was used as cathode material, and was spread on an aluminium sheet with PVDF as binder.

Two cylindrical batteries were made with carbon anode, $LiCoO_2$ cathode, and $LiPF_6$ dissolved in EC + DMC as electrolyte. The dimensions of the batteries were: (1) A-size, diameter = 16 mm, height = 50 mm, and (2) 8 A h class battery, diameter = 44 mm, height = 108 mm (see Fig. 2).

Three commercial batteries were used for comparison:

Commercial A: Produced by ‘Matsushite Battery Industrial’, size: diameter = 17 mm, length = 50 mm (17500 type).

Commercial B: Produced by ‘Sanyo Electric’, size: diameter = 18 mm, length = 65 mm (18650 type).

Commercial C: Produced by ‘Sony’, size: diameter = 18 mm, length = 65 mm (18650 type).

The charge/discharge examination was performed at −20, 0, 21, 40, and 60°C. The charging was conducted with a constant current of 0.8 C (e.g., 600 mA), which increased the voltage from 2.5 to 4.1 V. The upper voltage was kept constant at 4.1 V until the discharge. The latter was conducted at a constant current of 0.8 C.

Electrochemical characteristics at various charge/discharge rates (0.8 C, 1.6 C, 3.2 C, and 4.0 C) were also investigated at 21°C.

3. Results and discussion

3.1. Li-ion cylindrical (A-size)

Fig. 3 shows the discharge profiles of $LiCoO_2$/VGCF at 0.8 C (21°C). Batteries of the types $LiMn_2O_4$/VGCF and $LiNiO_2$/VGCF were also prepared to compare their charge/discharge characteristics with those of the $LiCoO_2$/VGCF system. As shown in Fig. 3, lithium intercalation/deintercalation into/from these oxides takes place at a potential of about 4 V. With $LiCoO_2$, the polarization is smaller and the capacity larger, when compared with other transition metal oxides [5]. The average discharge voltage was 3.65 V in the $LiCoO_2$/VGCF battery. Cycle characteristics up to 1000 cycles in each battery are shown in Fig. 4. All batteries showed high cyclability. The $LiNiO_2$/VGCF battery showed little fading in capacity. For this $LiNiO_2$/VGCF battery, an irreversible capacity at the initial cycle may affect cyclability, although this explanation is merely tentative. The cathode solubility in EC + DMC $LiPF_6$ decreases in the order: $LiMn_2O_4 > LiCoO_2 > LiNiO_2$. The $LiCoO_2$ phase is thus the choice material

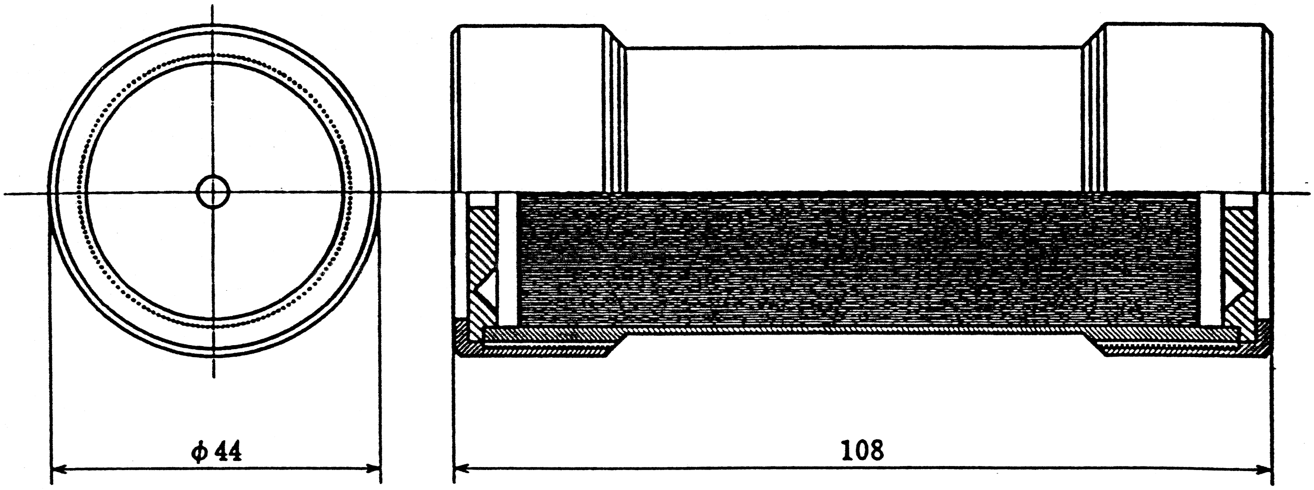

Fig. 2. Design of Nikkiso's Li-ion battery class 8 A h.

with respect to dissolution, ease of synthesis, and safety issues.

The good cyclability is explained by the formation of a good passivation layer at the EC/DMC/$LiPF_6$ interface, as well as by the good properties (mechanical, volemic, and ionic) of VGCF during intercalation/deintercalation.

Fig. 5 shows the charge/discharge profiles of $LiCoO_2$/VGCF at various temperatures and for a current density of 0.8 C (at 25 cycles). Although the capacity at −20°C was lower, discharging capacity did not strongly depend on temperature. Further, cycle characteristics at each temperature are also shown in Fig. 6. High cyclability was obtained at all temperatures. Self-discharge was investigated at three temperatures (21, 40, and 60°C). The measured self-discharge was 8, 15 and 31% per day at 21, 40, and 60°C, respectively. Self-discharge thus increases with temperature. However, this self-discharge becomes reversible after ∼25 cycles. This good result is directly related to the chemistry of carbon as the anode material. VGCF accommodates well solvent shuttles during self-discharge.

Fig. 7 shows the charge/discharge profiles of the $LiCoO_2$/VGCF battery at various charge/discharge rates. Thus, the lithium-ion rechargeable battery can be quickly and simply charged to the limiting maximum charging voltage. The rapid charge/discharge of this battery is due to the high diffusion coefficient of Li into VGCF [4]. Moreover, the relationship between charge/discharge rate and energy density (W h/kg) at the 25th cycle is shown in Fig. 8. Little capacity fading was observed at high current density. High cyclability was obtained for all current densities.

Fig. 9 compares the energy density of Nikkiso's Li-ion batteries with those of three commercial Li-ion batteries produced by other Japanese manufacturers. The compari-

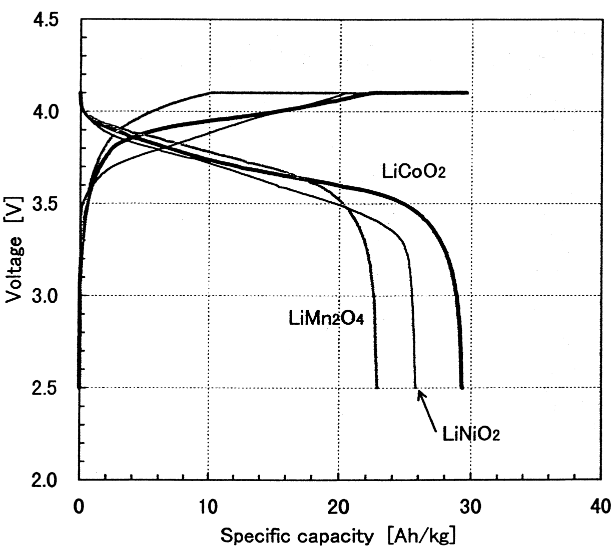

Fig. 3. Charge/discharge profiles of $LiCoO_2$/VGCF, $LiMn_2O_4$/VGCF, and $LiNiO_2$/VGCF batteries.

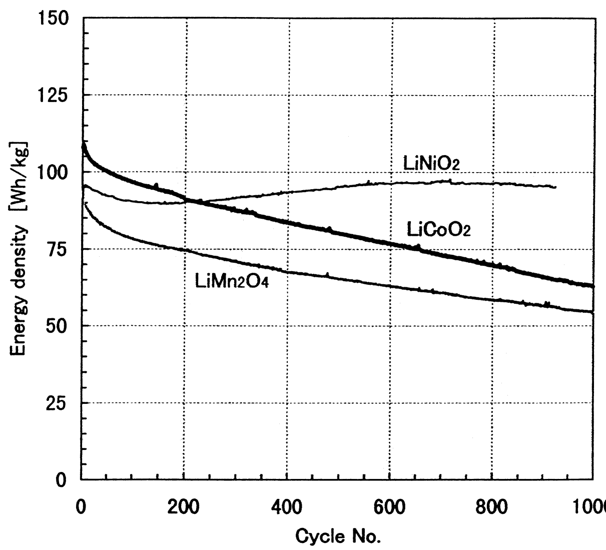

Fig. 4. Cycle characteristics of $LiCoO_2$/VGCF, $LiMn_2O_4$/VGCF, and $LiNiO_2$/VGCF batteries up to 1000 cycles at 0.8 C charge/discharge rates.

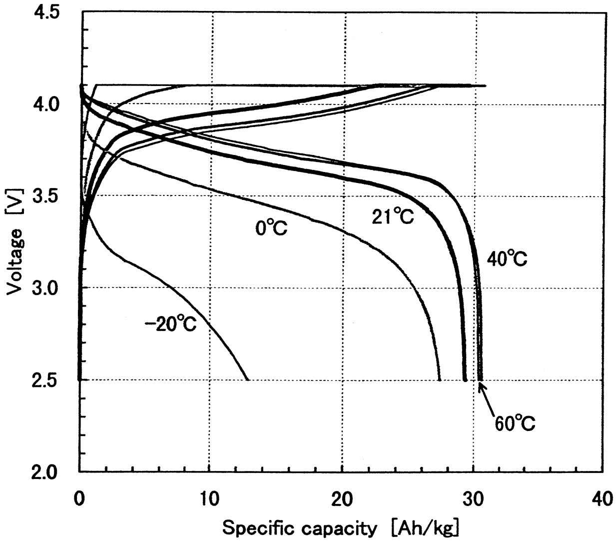

Fig. 5. Charge/discharge profiles of $LiCoO_2$/VGCF batteries at various temperatures.

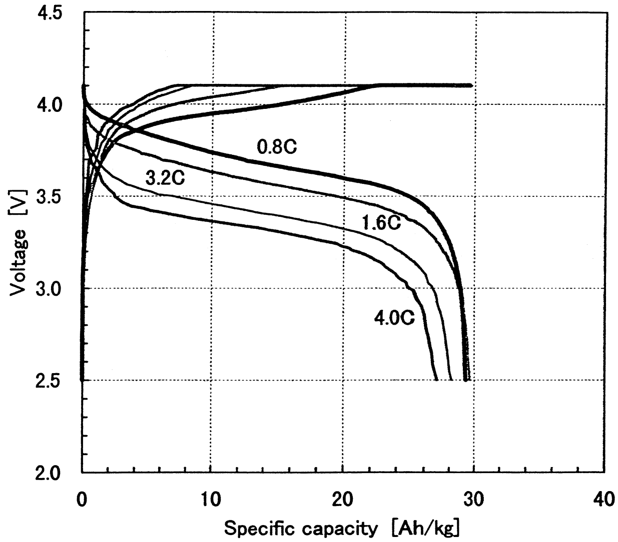

Fig. 7. Charge/discharge profiles of $LiCoO_2$/VGCF batteries at 21°C for various rates.

son is made in two temperature ranges: low (−20 to 0°C) and high (21 to 40°C) temperatures. Nikkiso's Li-ion battery performs better than the three commercial Li-ion batteries in the low-temperature range. This naked difference is linked to Nikkiso's VGCF superior anode material. This material has a good performance and a good capacity during intercalation/deintercalation in this low-temperature range. The VGCF-made carbon gauze is a highly conductive electrode in this temperature range. Consequently, this Nikkiso Li-ion battery is well suited for low temperature applications, such as Mars exploratory project. In the high-temperature range (21 to 40°C), Nikkiso's cell performance is surpassed only by that of commercial cell C among the cells investigated.

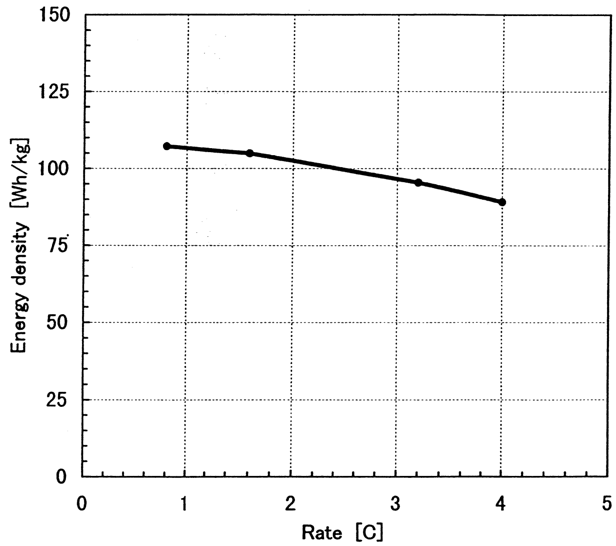

Fig. 8. Energy density dependence on charge/discharge rate.

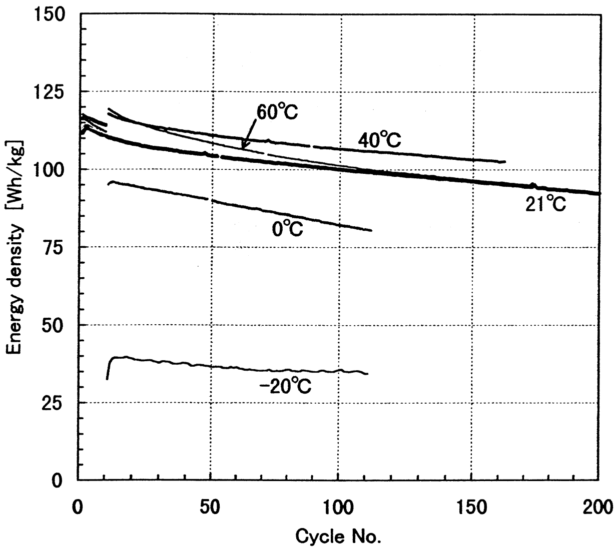

Fig. 6. Cycle characteristics of $LiCoO_2$/VGCF at various temperatures.

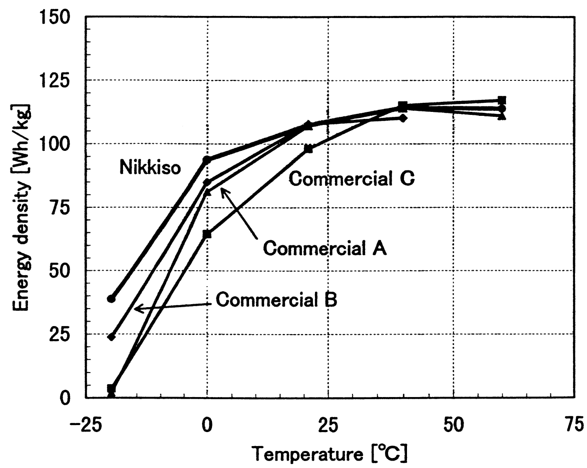

Fig. 9. Effect of temperature on electrochemical performance of Nikkiso's and commercial batteries at 0.8 C.

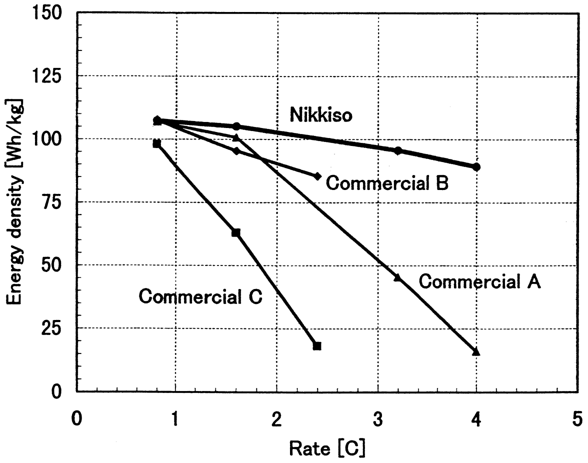

Fig. 10. Charge/discharge rate-dependence of energy density at 21°C; comparison of Nikkiso's battery with commercial batteries.

Fig. 10 compares the charge/discharge rate-dependence of energy density of Nikkiso's Li-ion cell with those of the commercial cells. We observe that the energy density of cells A and C decreases drastically as the current density increases. Cell B also suffers a decrease in its energy density as the current density increases, but to a lesser extent. Nikkiso's Li-ion cell, on the other hand, shows good performance and little decrease in energy density as the current density increases. This superior behavior is a direct result of the excellent performance of VGCF as a high charge/discharge-rate electrode [5].

Fig. 11 shows a Ragone plot of Nikkiso's and Sony's Li-ion cells at 20 and 0°C. Li-ion batteries have much

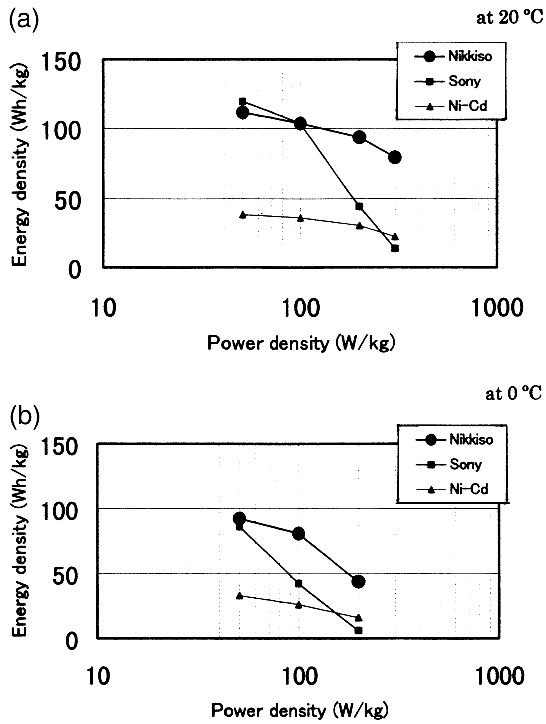

Fig. 11. Ragone plot of Nikkiso's and Sony's Li-ion, and Ni–Cd batteries. (a) At 20°C, (b) at 0°C.

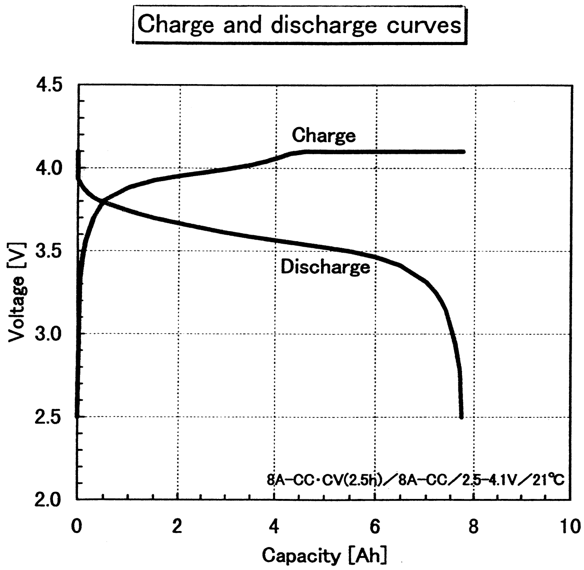

Fig. 12. Charge/discharge cycle of a Nikkiso 8 A h-class battery at 21°C.

higher energy densities than Ni–Cd batteries. The Li-ion rechargeable battery shows an average high voltage of about 3.6 V, which is three times as high as that of the Ni–Cd battery. When an application requires an operating voltage ranging from 3 to 4 V, three Ni–Cd batteries connected in series are required. Only one Li-ion rechargeable battery would be needed for the same application. Moreover, the monitoring of the remaining discharge capacity of Li-ion batteries would be possible because of the gradually decreasing cell voltage during discharge.

At 20°C, Nikkiso's Li-ion cell performs better than Sony's cell. At 0°C and high power density, Nikkiso's Li-ion cell has a higher energy density than the other cell. The difference between Sony's and Nikkiso's technologies lies in Sony's use of a hard carbon anode prepared with a

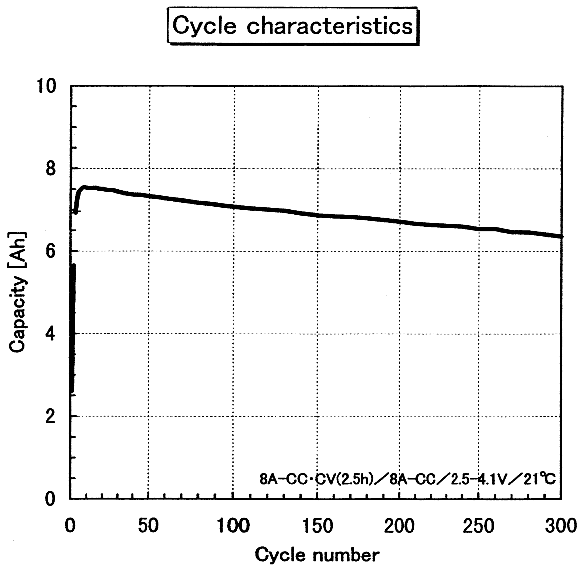

Fig. 13. Cycle performance of Nikkiso's Li-ion rechargeable battery (8 A h-class).

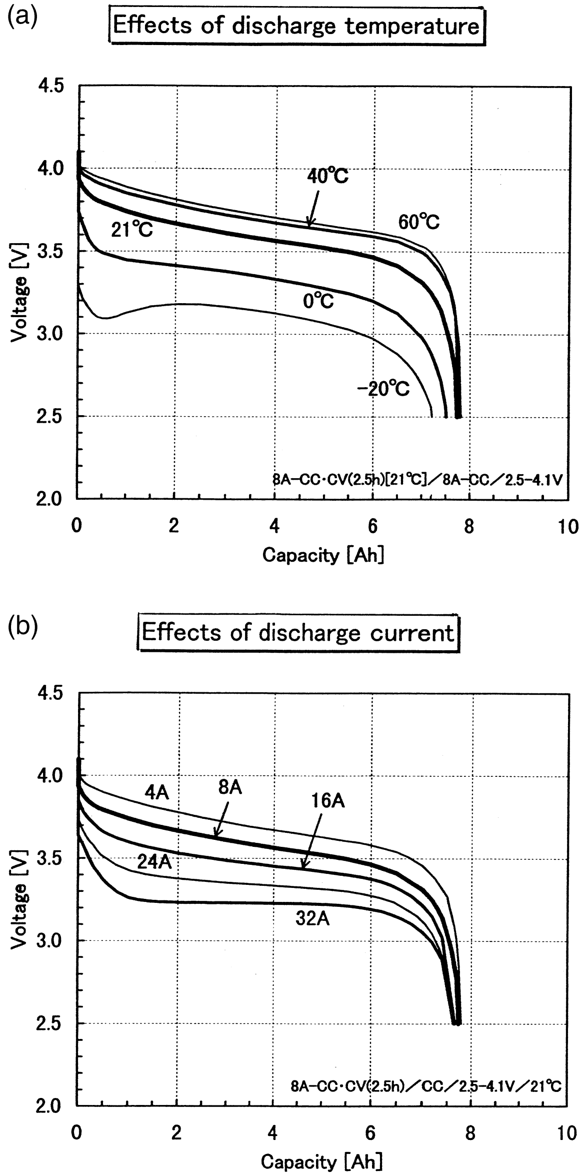

Fig. 14. Effect of temperature (a) and current density (b) on discharge capacity of an 8 A h-class battery.

polyfurfuryl alcohol as precursor. This electrode has a sloping voltage upon discharge and a rated capacity of about 350 mAh/g when charged. Unlike Sony's electrode, Nikkiso's VGCF graphitic carbon electrode induces a flat voltage, with a rated capacity of 363 mAh/g when charged. This capacity is close to that of LiC_6 (372 mAh/g). Accordingly, graphitic carbon such as VGCF makes a practical anode material for Li-ion rechargeable batteries [1–4].

A cell with a capacity of 8 A h was used and discharged to 2.5 V. VGCF and $LiCoO_2$ were used as negative and positive electrodes, respectively. The current applied was 8 A. The discharge capacity was close to the nominal capacity of 8 A h (Fig. 12). The medium voltage was about 3.6 V. Fig. 13 shows the capacity dependence upon cycle number. At C/1, the cell achieves 300 cycles and retains a capacity of about 90% of the initial value. These data were obtained at 100% DoD (depth of discharge). By cycling with small DoD and with Electric Bicycle profile, the battery cyclability can be further extended. The performance of 8 A h class batteries at various temperatures is displayed in Fig. 14a. The discharge capacity at 21°C is lower than those obtained at 40 and 60°C. At −20°C, however, the capacity is about 7.1 A h, which is very close to the nominal capacity. Fig. 14b shows that the discharge current at 21°C has little dependence on the discharge capacity.

Table 1
Performance of Nikkiso's $LiCoO_2$/VGCF battery at 21°C

Cell size		Performance[a]	
Diameter	16.5 mm	Capacity	763 mAh
Height	49.3 mm	Discharge voltage	3.65 V
Volume	10.8 ml	Energy capacity	2.79 W h
Weight	26.0 g	Energy density	107 W h/kg (258 W h/L)

[a] Data at the 25th cycle.

4. Conclusion

Cylindrical batteries using VGCF as anode material were constructed. The performance of the $LiCoO_2$/VGCF battery at 21°C are summarized in Table 1. In this battery system, high capacity (763 mAh) and high energy density (107 W h/kg or 258 W h/L) were obtained. Further, high cyclability was also obtained at all temperatures and current densities investigated.

At low temperatures (−20 to 0°C), Nikkiso's Li-ion batteries show a good performance. This technology is thus well suited for use in space applications. A Ragone plot shows that Nikkiso's batteries made with VGCF anodes offer a better performance than that of Sony's batteries at 0 and 20°C. Nikkiso's batteries perform very well at high current density. This technology is desirable for PNGV application. Preliminary results with an 8 A h-clan battery for electric bicycle (EB) are encouraging. Continued investigation is underway to assess the battery's performance with respect to the EB protocole.

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